ON THE USE OF PHOSPHATES TO INHIBIT OXIDATION OF INDUSTRIAL CARBONS

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I. INTRODUCTION

The use of additives to inhibit the oxidation of carbon-graphites has been well-known in the industry for many years. Among the earliest to report on the use of phosphorus-containing additives was Wicke [1]. He studied the effect of phosphoryl chloride which was added to the gas phase during oxidation. Others who have examined the effects of oxidation-inhibiting additives include Arthur [2,3], Hadman et al [4], Day [5], and Hedden [6].

The exact mechanism by which phosphates, in particular, inhibit the oxidation of carbon is still a moot question. However, it is generally agreed that both chemical and physical processes are involved. That is, the phosphate covers potentially active sites on the carbon surface both by a strongly chemisorbed layer [7] and/or a physical barrier of either a glassy or crystalline nature as in the case of some oxides [8]. The latter would appear to be the case in the work reported by Paxton [9].

Factors which determine the effectiveness of a given phosphate treatment include the chemical composition of the impregnant, the molar concentration of the starting solution, the amount of material finally deposited within the pore system of the carbon, the distribution of the treatment within the carbon, and the reactivity of the original carbon-graphite [10-13]. Of importance also is the permeability of the original carbon to the solution or liquid used for the impregnation.

The oxidation of untreated carbon at some temperature is usually expressed as the Specific Reaction Rate [14, 15]. That is, weight loss per unit time per unit area [15]. The area used to calculate the rate may be the geometric or apparent surface area of the sample [14], the B.E.T. or nitrogen adsorption area, or some fraction of the total surface area [16]. There are certain advantages and shortcomings involved in the use of all of these [1, 17]. The rate of reaction is known to be dependent upon both chemical and diffusional mechanisms [18]. In addition, the rate of oxidation of an untreated carbon at temperature below 1800°F may be strongly affected by the nature of the carbon itself. Such variables as heat treatment history, impurity content, crystallinity, porosity, and permeability are all inherent properties of the sample material which can, in fact, influence the rate of oxidation [14, 17, 19].

In the case of a treated material, an additional set of variables (mentioned earlier) are introduced which are concerned with impregnant and its interaction with the base material. These new variables are then added to the list given above to produce the entire collection of factors which may be changed so as to affect the resulting reaction rate of treated carbon with oxygen. It is obvious that the system must be simplified greatly by making many of these quantities a constant before meaningful data may be obtained on the reaction.

The work described in this paper concerns the evaluation of phosphate impregnants for improving the oxidation resistance of commercial carbon-graphites. Impregnation of the carbon may be done by a variety of methods including molten

salts, water-or acid-based solutions, and vapor deposition. The technique used to treat the materials described was a solution impregnation via a vacuum-pressure cycle. The objective herein is to examine the experimental results and discuss some of the factors which make these phosphate treatments effective inhibitors of the oxidation of carbon.

II. EXPERIMENTAL

The TGA equipment used in this work is shown in Fig. 1. It is simply an electrobalance (Cahn RH) mounted above a vertical tube furnace. The sample is suspended within the furnace, from the balance, on a Mullite rod and the sample weight is continuously recorded as the material is burned off. The furnace control is such that the temperature may be varied with a preselected program or held constant. For the purpose of this work, the furnace temperature was held constant at 1200°F for all the runs in order to minimize the variables described earlier.

The samples were preheated in nitrogen before the oxidizing gas was admitted into the tube furnace. For this work, only air was used to burn the samples. The equipment, however, includes the necessary metering system to feed various oxygen-nitrogen mixtures into the furnace, if required.

The test data are reported as the time required for ten percent burnoff of the sample under test. With certain qualifications, the longer it takes the material to lose ten percent of its original weight, the more effective is its oxidation resistance (OR).

All samples used were in the form of 3/4-inch cubes. With a few exceptions, the same base material was used for all tests in order to minimize the variation of the data due to the reactivity of the carbon.

III. RESULTS

Table I is a compilation of the primary experimental data to be discussed in this paper. Some additional data will be presented later to clarify particular points. The base grades and treatments are given letter names because the nature of these materials is not vital to following the discussion.

TABLE I
EXPERIMENTAL RESULTS FOR 1200°F IN AIR

Base Grade	Treatment[3]	% Treatment	Hours to 10% Burnoff*
G[1]	None	-	0.08
G	A	10.4	54
L[2]	None	-	3.4
L	A	7.5	54
L	B	4.65	103
L	C	8.2	106
L	D	9.0	134
L	E	12.6	36
Glassy Carbon	None	-	10.5

1 = graphitized material, pitch-bonded natural graphite
2 = graphitized material, pitch-bonded lampblack
3 = all treatments are metallic phosphates

*Average values

IV. DISCUSSION

The data given in Table I represent average values for a number of samples of each material. This is a point worth emphasizing since the spread in experimental data is usually about 20 percent. Therefore, a reliance upon only a few data points may be very misleading when one draws conclusions concerning the OR effectiveness of a given treatment and/or material.

A.   Uniformity of Treatment:

It is usually not sufficient to know only how much of a given treatment is deposited in the carbon (percent pickup), but one should also have some information concerning the distribution of the impregnant within the carbon. To exemplify this point, data are presented in Fig. 2, which resulted from successive weighing and grinding of a number of treated cubes. It is clear from the curves in Fig. 2 that the local concentration of impregnant decreases toward the center of the cubes. Several reasons for this uneven distribution may be suggested: first, the degree to which the impregnant penetrates the sample is determined by the permeability of the carbon and the viscosity of the solution; and, second, the uniformity of the treatment may be adversely affected if the impregnant is a suspension and not a true solution. If the suspension is coarse enough, the solid particles may be filtered out and only the clear liquid may, in fact, reach the center of the sample. It is noted, however, that treatments used in this work were true solutions. Another reason suggested for this concentration gradient within the treated carbon is that when the treated material is being dried, the impregnant may migrate toward the surface of the sample. Whatever the reason, it is clear that, for the data shown in Fig. 2, there is a concentration gradient. The effect that this has on OR is obvious if the treatment is in the form of a shell and if the oxygen penetrates the pore system beyond the treated shell. Therefore, a large amount of treatment does not necessarily insure a high OR. An exception to this occurs when the pores are physically blocked as seems to be the case for the molten salt treatments described by Paxton [9].

B.   Hygroscopic Behavior:

A characteristic of many phosphate treated carbons, which is undesirable from the viewpoint of product use, is the tendency to absorb moisture and ultimately exude droplets of sticky liquid from the pore mouths. It is this behavior that rules out the use of a number of treatments which are, in fact, quite effective in inhibiting the oxidation reaction. For example, the material called "Treatment D" (line 5, Table I) is quite reasonable as an OR treatment. However, the treated carbon becomes tacky and moist after several days in room air.

An improvement can be made with coatings, cure cycles, and storage conditions in that some delay can be realized in moisture pickup. These measures, however, usually do not eliminate the problem. The solution is, of course, to find a phosphate treatment which is not hygroscopic while, at the same time, it possesses excellent OR properties.

While certain phosphate compounds such as those of tungsten and molybdenum are apparently hygroscopic, it also is possible that some other treatments exhibit this behavior because of excess phosphoric acid within the finished piece. Therefore, in evaluating the moisture pickup behavior of phosphate treatments, it is advisable to consider the excess acid present, if any.

C. Glassy and Crystalline Phosphates:

Another property of the phosphate treatments which increase the OR of carbon is the structure of the material deposited on the surface of the carbon. Many treatments examined in this work were obviously glassy or crystalline (grainy) when examined visually, after cure. In general, it was found that glassy deposits offered more protection to the carbon than did those which appeared grainy and discontinuous. This fact would tend to support the view that the oxidation is inhibited by means of a physical barrier of phosphate glass between the carbon surface and the oxidizing gas. This is shown in Table I, as line 7 (glassy deposit) and line 8 (grainy deposit) with 134 and 36 hours to 10 percent, respectively.

D. Stability of the Treatment:

One of the more obvious points which can be made in this discussion is that the particular phosphate used as an impregnant must be stable at the test temperature. To prove that the interaction between the carbon surface and the phosphate material does not change the stability of the treatment, several compounds known to be unstable at 1200°F were run and the OR, measured as time to 10 percent weight loss, was very poor (less than 24 hours).

E. Reactivity of the Carbon:

The results from this work indicate that with treatment levels used in the samples tested for OR, the impregnant does not completely mask the reactivity of the basic carbon material. In the case of the untreated natural graphite grade G, the reactivity was so high that it ignited at 1200°F in air. On the other hand, the untreated lampblack material L did not, in fact, ignite, although the sample temperature rose about 40°F above the furnace temperature. These results are given in Table I in lines 1 and 3, respectively. The meaning of these results is that the natural graphite-based material was of such a reactivity that the heat-release rate greatly exceeded the heat-loss rate. Thus the sample temperature rose to the ignition temperature and from there to the maximum obtainable temperature which, in this case, would be in the bulk-diffusion combustion region, or Zone III. The lampblack-base material was less reactive and showed none of the behavior described above. For a detailed explanation of the significance of this behavior, the reader is referred to an excellent text by Vulis [20].

The same treatment was given each of these base grades and the treated pieces were then tested for OR. As expected, the treated grade G reacted faster than the treated grade L (lines 2 and 4, Table I), even though the former contained almost twice the amount of treatment as the latter.

When industrial carbons are oxidized, it is generally agreed that there is usually a preferential attack on the binder [21]. In the oxidation of phosphate treated carbons, similar results have been noticed. Here again, at the treatment levels used in this work, the phosphate failed to completely mask off the basic reactivity of the materials.

For the purpose of completeness, glassy carbon material was also oxidized (line 9, Table I). This impervious material ran 10.5 hours to 10 percent weight loss. It would seem that from the viewpoint of OR, phosphate-coated glassy carbon would be quite acceptable. In a practical sense, however, application and fabrication problems would make this an unlikely choice.

V. CONCLUSIONS

When evaluating phosphate treatments for oxidation resistance, one should have information not only on the total amount of treatment within the carbon but the distribution of that treatment as well. Such information could help to explain results which otherwise would appear quite contradictory.

The factors which determine the effectiveness of a particular OR treatment, other than percent pickup and distribution, include the glassy properties of the treatment, the thermal stability of the compounds formed at the test temperature (1200°F in this work) and, in some cases, the reactivity of the base grade.

Properties other than OR may disqualify an impregnation from being considered for commercial use. In the case of phosphates, the tendency to exude a sticky solution is usually the most troublesome behavior.

VI. REFERENCES

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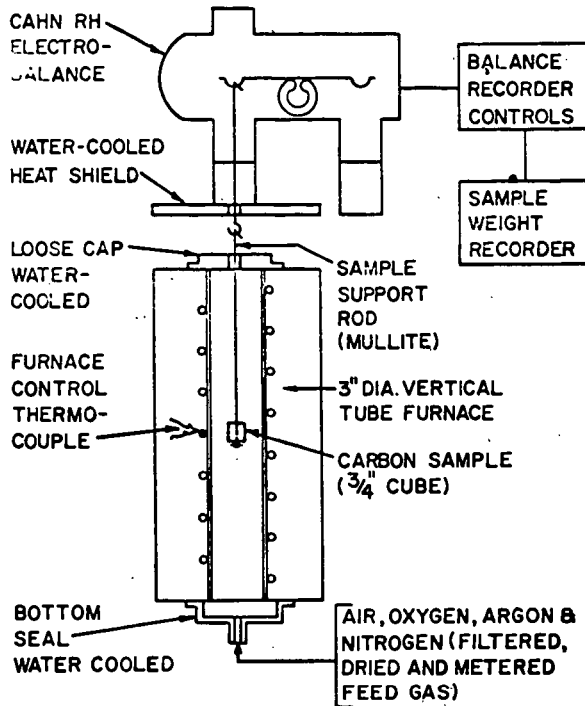[21] Froberg, R.W., Ph.D. Thesis, The Pennsylvania State University, 1967.

CAHN RH
ELECTRO-
BALANCE

BALANCE
RECORDER
CONTROLS

WATER-COOLED
HEAT SHIELD

SAMPLE
WEIGHT
RECORDER

LOOSE CAP
WATER-
COOLED

SAMPLE
SUPPORT
ROD
(MULLITE)

FURNACE
CONTROL
THERMO-
COUPLE

3" DIA. VERTICAL
TUBE FURNACE

CARBON SAMPLE
(3/4" CUBE)

BOTTOM
SEAL
WATER COOLED

AIR, OXYGEN, ARGON &
NITROGEN (FILTERED,
DRIED AND METERED
FEED GAS)

FIG. I OXIDATION RESISTANCE TEST SYSTEM

10.0

LOCAL
WEIGHT
PERCENT
TREATMENT

5.0

CUBE
SURFACE

ASSUMED

0

0   0.1   0.2   0.3   0.4

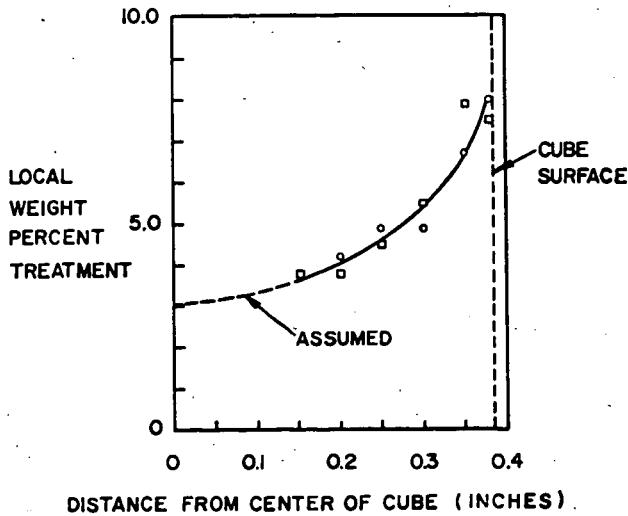DISTANCE FROM CENTER OF CUBE (INCHES)

FIG. 2   LOCAL DISTRIBUTION OF PHOSPHATE
         TREATMENT WITHIN CUBE OF GRADE L
         (LAMPBLACK BASE)